A project report

on

SYNTHESIS AND CHARACTERISATION OF COPPER NANOPARTICLE-GRAPHENE COMPOSITE

Submitted by

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ABSTRACT

A Copper nanoparticle based composite with graphene oxide have prepared. The Cu/GO nanocomposite was characterised by XRD and SEM technique. As graphene based nanocomposite have several important application like Photocatalyst, Sensor, Energy storage material, Fuel cell and Environmental issues as well as also in some Organic coupling reactions and in biological field so the present work could be considered as a potential for some novel application.

INTRODUCTION

Graphene has been considered as an excellent suitable catalytic support due to its high thermal conductivity [1], good mechanical strength [2], electrical conductivity [3], and large specific surface area (SSA) [4]. Graphene based metal and metal oxide nanocomposite have been used in electrocatalysis, photocatalysis, bio and chemosensors and in carbon-carbon bond formation. Earlier it has been reported that graphene can enhance the catalytic activity of a catalyst by means of increasing the catalytic surface area, efficient capping and protection of catalyst materials, and efficiently storing and shuttling electrons through the sp^2 hybrid 2D carbon network.[5,6] However, developing homogeneous composites with a uniform distribution of catalyst and controlling the catalyst loading remains a major problem. This is a very challenging task due to the poor solubility of graphene and the weak interactions between graphene and catalyst. Chemically synthesized graphene from colloidal graphene oxide offers significant advantages in producing soluble graphene and graphene based catalyst composites.[7] Metal and semiconductor nanoparticles have been loaded on to graphene by using chemical functional groups on the graphene surface,[1,5] electrostatic interactions,[3] hydrophobic interactions30 and via functionalization of graphene. However, these catalyst composites mainly focus on electrocatalysis that involves electron transfer reactions and only limited studies have been performed on other types of catalysis.[6,7] C–N bond formation via transition metal based catalysis is currently a subject of great interest and intensive research is being carried out to achieve useful organic transformations.[8-9] Photoinduced cross-coupling reactions by metal nanocomposite is also a very important

research work now a days. Copper catalysed cross coupling reactions and arylation reactions have been recognised as a reliable pathway for carbon-carbon bond formation process as copper is cheap, nontoxic and ease of loading on catalytic support. So in this work the main focus was given to synthesise Copper nanoparticles (Cu^0) loaded graphene composite for some photomeadiated cross coupling reactions.

EXPERIMENTAL SECTION

Synthesis of graphene oxide (GO):

Graphene oxide was prepared from purified natural graphite powder according to the hammors method. In details graphite powder (1.0 g), NaNO3 (0.5 gm) and $KMnO_4$ (3.0 g), were slowly added to a concentrated H_2SO_4 solution (23 mL) within an ice bath. After removing the ice bath, the above mixture was intensely stirred at 35^0 C for 30 minutes. After the reaction was completed, deionised water (46 mL) was added to the above mixture while keeping the temperature at 98^0 C for 15 minutes, followed by reducing the temperature to 60^0 C with the addition of warm deionised water (140 mL) and H_2O_2 (30 % , 10 mL) while stirring continuously for further 2 hours. The obtained mixture was centrifuge to collect the solid product and washed with 4 wt % HCl solution 5 times and then with deionised water until the PH of the supernatant was neutral. Finally the material was dried to obtained a loose brown powder.

Synthesis of Graphene:

Graphene was prepared by the reduction of GO using hydrazine under heating conditions. About 40 mL of aqueous GO solution (1 mg mL^{-1}) were mixed with 400 mL hydrazine and heated for 2 h at 80^0C under stirring conditions. Then the precipitated graphene was washed with water, ethanol and dried under vacuum.

Synthesis of Copper nanoparticles:

Required amount of copper sulphate (0.255 gm) was dissolved in 10 mL of ethylene glycol at 70^0 C. After that the solution $N_2H_4.H_2O$ (80 Vol %, 20 mmol) was added dropwise with intensive stirring. Stirring was carried out for 10 minutes. Further 1.0 (M) NaOH was added up to PH 10-12. The precipitate formed was washed with distlled water, ethanol and acetone.

Synthesis of Copper nanoparticle-Graphene (Cu-G) composite:

About 120 mL of an aqueous graphene oxide (90 mg) solution was prepared having a a graphene oxide concentration of 0.5-0.8mgmL^{-1}. Next 10 mL of 0.003 (M) copper acetate (54 mg) were added under stirring condition. After one hour of stirring, 600 μL of hydrazine followed by the appearance of a black precipitate after 90 minutes. Heating was continued for 2 hours and then the precipitated Cu-G composite was washed with water, ethanol and dried under vacuum.

CHARACTERISATION:

The as synthesised catalysts were characterise by X-ray diffraction (XRD) (Rikagu Japan/Ultima-IV) by Cu Kα radiation in 2θ ranging from 10^0 to 70^0 and scanning electron microscope (SEM) (BRUKER).

RESULT DISCUSSION:

X-ray diffraction method (XRD):

The phase composition diagram of the nanocomposite has been investigated from X-ray diffractrometry. The mean size of the nanoparticles can be calculated from Scherer's equation

$$d = \frac{0.9\lambda}{\beta\cos\theta}$$

The highly intense reflection of Cu/graphene nanocomposite had indicated that the copper nanoparticles have grown uniformly over graphene sheet. The XRD image had shown in figure 1.

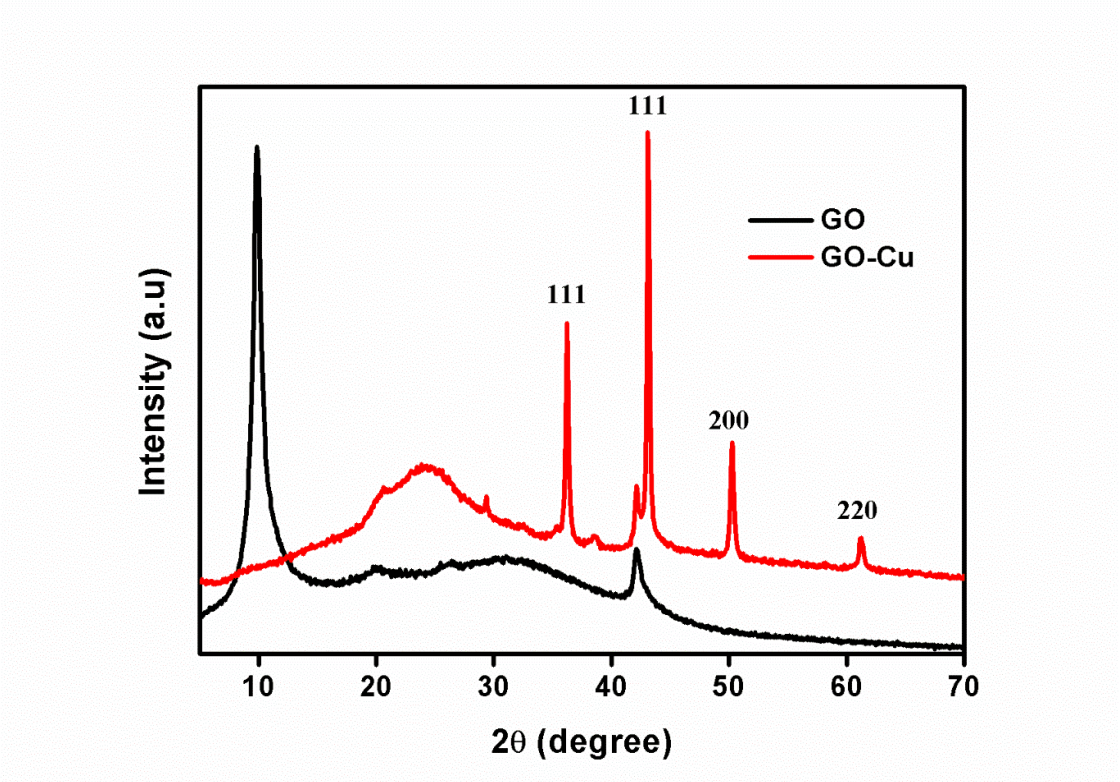

Figure 1 XRD images of Cu/grapheme nanocomposite

Scanning electron microscopy (SEM):

The microstructure and the morphology of the nanocomposite has been showed in figure 2 (a) and 2 (b). From the SEM images it could be clearly observed that the Cu nanoparticles was uniformly deposited over the Graphene layered nanostructured. The sheet like morphology of graphene was also an advantage for catalytic activity which was clearly visible from the SEM micrographs.

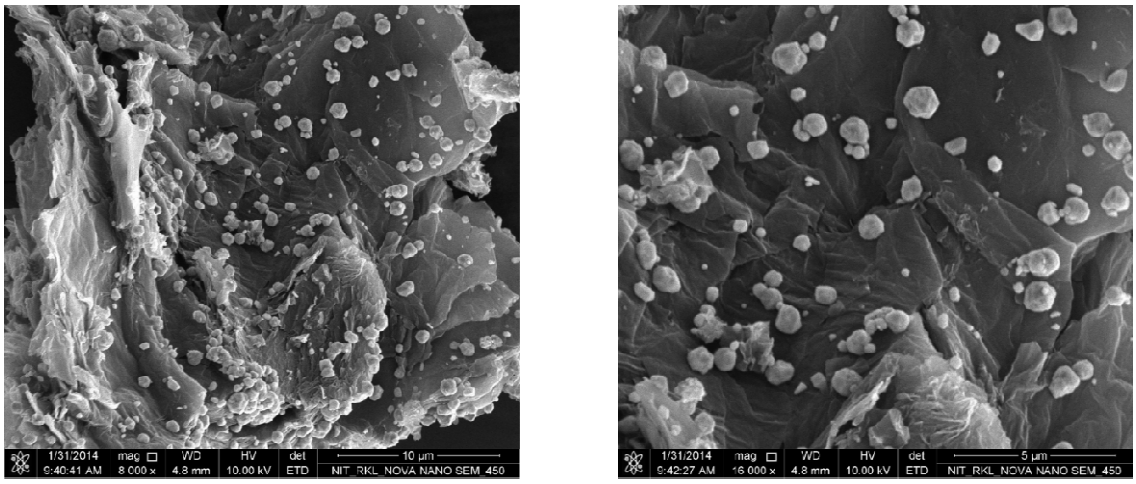

Figure 2 (a) and 2 (b) represents the low and high resolution SEM images respectively of Cu/graphene nanocomposite

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